

Global secondary organic aerosol from isoprene oxidation

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[1] Inclusion of isoprene as a source of secondary organic aerosol (SOA) in a global model increases the global burden of SOA from all sources by more than a factor of two. The isoprene source substantially increases SOA concentrations in the free troposphere, because isoprene, and, more importantly, isoprene's oxidation products, have much greater concentrations at higher altitudes than other biogenic SOA precursors, highlighting the importance of semi-volatile organics for SOA formation. These results are robust with respect to increases in partitioning of non-isoprene oxidation products at higher altitudes and increased wet removal of isoprene oxidation products. This additional source of SOA enhances production of SOA from other parent hydrocarbons by 17%, and leads to an overall distribution of SOA that differs enough from previous predictions to warrant reevaluation of the radiative effects of organic carbon aerosol. **Citation:** Henze, D. K., and J. H. Seinfeld (2006), Global secondary organic aerosol from isoprene oxidation, *Geophys. Res. Lett.*, 33, L09812, doi:10.1029/2006GL025976.

[2] Secondary organic aerosol (SOA), formed when oxidized products of volatile hydrocarbons condense, often comprises a substantial portion of the organic mass fraction of atmospheric aerosols. The prevalence of organic carbon aerosol on a global scale makes identifying significant sources of SOA an important task, as carbonaceous aerosol is known to strongly influence air quality and climate change. Model predictions of organic carbon aerosol concentrations have exhibited a low bias not present in coincident predictions of black (elemental) carbon, with this bias being attributed to under-prediction of SOA [Heald *et al.*, 2005; Tsigradis and Kanakidou, 2003].

[3] Isoprene (C_5H_8) is the second most abundant hydrocarbon emitted into the Earth's atmosphere after methane (~ 500 Tg yr^{-1} [Guenther *et al.*, 1995]). Although it has long been assumed that all its products remain in the gas phase, if isoprene were to yield even a small amount of aerosol, this would have a profound effect on global sources of organic aerosol. Biogenic volatile organic compounds other than isoprene, such as terpenes and sesquiterpenes, are presently believed to be the largest source of SOA mass on a global scale, with model estimates of the magnitudes of these sources ranging from 12–70 Tg yr^{-1} [Kanakidou *et al.*, 2005]. Recent laboratory chamber studies of isoprene photooxidation show that SOA yields are 1–2% at high NO_x levels [Kroll *et al.*, 2005] and $\sim 3\%$ at low NO_x levels [Kroll *et al.*, 2006]. Furthermore, organic aerosol collected

in forested areas is strongly indicative of an isoprene precursor [Claeys *et al.*, 2004a, 2004b; Ion *et al.*, 2005; Kourchev *et al.*, 2005; Matsunaga *et al.*, 2003]. The impact of such a potentially large source of carbonaceous aerosol necessitates careful investigation of the fate of isoprene oxidation products on a global scale.

[4] Claeys *et al.* [2004b] estimated SOA production from isoprene to be 2 Tg yr^{-1} by simply multiplying an estimate of global isoprene emissions by an observed yield of condensed polyols from isoprene; subsequent recognition of additional SOA production pathways increases this estimate [Claeys *et al.*, 2004a]. Cloud processing of isoprene oxidation products alone has been calculated to contribute 1.6 Tg yr^{-1} of SOA [Lim *et al.*, 2005]. Matsunaga *et al.* [2005] estimated a source of SOA from isoprene in the range of 10–120 Tg yr^{-1} ; however, this study neglects the effects of temperature and background organic particulate matter concentrations on gas - particle partitioning, factors known to strongly influence SOA formation.

[5] Recent availability of data from laboratory chamber studies of isoprene oxidation [Kroll *et al.*, 2005, 2006] allows us to now assess the global SOA forming potential of isoprene in a more fundamental manner. Several factors influence SOA formation, such as the ambient NO_x concentration, RO_2 concentration, temperature, and heterogeneous reactions [Limbeck *et al.*, 2003; Czoschke *et al.*, 2003; Edney *et al.*, 2005; Kroll *et al.*, 2006]. Until the mechanisms that govern these types of behavior are precisely known one must use empirical parameterizations based on actual laboratory data [Kanakidou *et al.*, 2005].

[6] For inclusion of SOA in global models, the framework of the two-product model [Odum *et al.*, 1996; Seinfeld and Pankow, 2003] provides a method for predicting the formation of SOA based upon empirical parameters determined from laboratory chamber studies even when the exact chemical nature of the aerosol products, or even the intermediate gas-phase oxidation products, are not known [Griffin *et al.*, 1999b]. The model describes the oxidation of a parent hydrocarbon to produce two representative gas-phase products with stoichiometric coefficients α_1 and α_2 . Subsequent partitioning of these products into the aerosol phase is governed by the availability of pre-existing organic aerosol and by their equilibrium partitioning coefficients, K_1 , K_2 , taking into account the temperature dependence of the partitioning coefficients using the Clausius-Clayperon equation. At the moment condensation onto other (non-organic) aerosol species is not considered, though this would afford increased SOA formation from all species [Tsigradis and Kanakidou, 2003].

[7] We simulate global SOA formation using the chemical transport model GEOS-Chem (version 7.2.4 with a horizontal resolution of $4^\circ \times 5^\circ$ and 30 layers up to 0.01 hPa, GEOS-3 meteorological fields [Park *et al.*, 2004]), previously implemented with a gas-particle parti-

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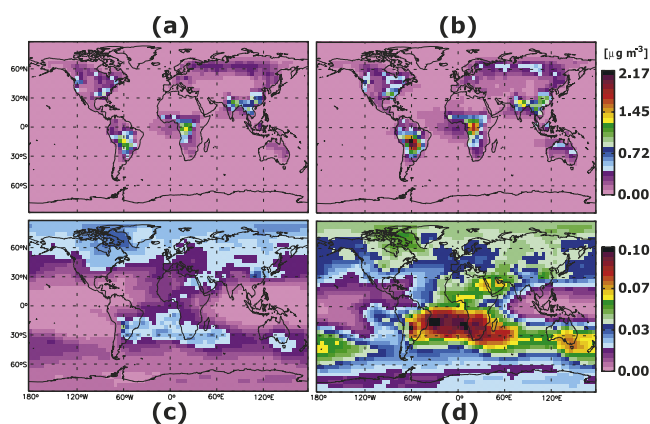


Figure 1. Yearly average total SOA concentrations during the year March 2001–Feb 2002 (a) at the surface without isoprene source, (b) at the surface with isoprene source, (c) at 5.2 km without isoprene source, and (d) at 5.2 km with isoprene source.

tioning model of SOA formation from terpenes [Chung and Seinfeld, 2002; Heald *et al.*, 2005], updated here to include formation of SOA from oxidation of isoprene using parameters shown in Table 1. The α 's and K 's were derived from the final amount of SOA formed in chamber studies of isoprene oxidation by OH [Kroll *et al.*, 2006] using the same method as Griffin *et al.* [1999a]. We assume reaction with OH is the only pathway for formation of SOA from isoprene. Though reaction with O_3 or NO_3 may also lead to SOA formation, the magnitudes of these sources are assumed to be minor, because an order of magnitude more isoprene reacts with OH than with O_3 or NO_3 on a global scale [Calvert *et al.*, 2000]. We assign a molecular weight of 130 for the oxidation products from isoprene, which is that of tetrol, a compound prevalent in SOA that originates from isoprene [Claeys *et al.*, 2004b].

[8] An issue with empirical partitioning models is that the conditions of the chamber studies from which the yield parameters are derived may not be representative of atmospheric conditions. The main concern has been that NO_x levels in these experiments tend to be larger than those in the troposphere. The experiments used to derive the yield parameters for isoprene given here were carried out under low NO_x concentrations (<1 ppb) and at cooler temperatures more relevant to tropospheric conditions [Kroll *et al.*, 2006]. Still, a single set of yield parameters may not fully represent SOA formation throughout the entire range of conditions present in the atmosphere—further laboratory and modeling studies are required to explicitly specify the dependence the SOA yield parameters on the chemical environment.

[9] Implementation of this model on global scales requires knowledge of thermophysical parameters that are not easily determined experimentally. The enthalpy of vaporization of SOA, ΔH_v , is critical for extrapolating the equilibrium gas-particle partition coefficients to colder temperatures [Tsigaridis and Kanakidou, 2003]. The value of ΔH_v depends upon the nature of the SOA and how it was formed [Offenberg *et al.*, 2006], though there is not yet enough experimental data available to justify the use of more than a single value of ΔH_v for all SOA. The base case

value of ΔH_v used here, 42 kJ mol⁻¹ [Chung and Seinfeld, 2002], originally considered a lower estimate in comparison to values from similar studies which ranged as high as 156 kJ mol⁻¹, is perhaps in fact quite reasonable, as recent experimental studies of the temperature dependence of SOA formed from α -pinene have placed ΔH_v closer to the lower estimates [Offenberg *et al.*, 2006; C. O. Stanier and S. N. Pandis, Measurements of the volatility of aerosols from alpha-pinene ozonolysis, submitted to *Environmental Science and Technology*, 2006]. The sensitivity of SOA predictions to the aqueous solubility of the oxidation product species, governed by an estimated average Henry's law constant of the oxidation products, H , has also been mentioned by Tsigaridis and Kanakidou [2003], though the consequences of variations in H on global SOA predictions have not yet been explored. Loss of these products by wet removal depends strongly on H . Given that polyols resulting from isoprene oxidation are more soluble than many of the previously identified species in SOA, which were taken to have an average Henry's law constant of 10⁵ M atm⁻¹ (R. Sander, Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry (version 3), <http://www.mpch-mainz.mpg.de/~sander/res/henry.html>), we consider the effect of increasing the Henry's law constant of the oxidation products to 10⁶ M atm⁻¹, and, for comparison, decreasing it to 10⁴ M atm⁻¹.

[10] Model predictions of global yearly average SOA concentrations for the year March 2001–February 2002 are shown in Figure 1. We select this time period because it encompasses the ACE-Asia campaign, for which the observed amount of organic carbon aerosol in the free troposphere exceeds predictions by the base case model by a factor of 10–100 [Heald *et al.*, 2005]. Figures 1a and 1c show the total concentrations of SOA generated by the existing (base case) biogenic VOCs (terpenes and OVOCs) at the surface and at 5.2 km, respectively. Figures 1b and 1d show total SOA concentrations when isoprene is included as an additional source of SOA. The difference between these two simulations is striking, most notably in the magnitude of the increases in the free troposphere, where typically more than 70% of the SOA is from isoprene. SOA concentrations increase by a factor of 1.5 to 3 in regions of relatively high SOA concentrations, and they increase by more than a factor of 10 in remote marine regions where SOA concentrations are small (<0.01 $\mu\text{g m}^{-3}$), such as the Indian and South Central Pacific oceans.

[11] The yearly average total SOA burden (B_T) and the net yearly SOA production (P_T) are given in Table 2, where the total production is also broken down into contributions from isoprene (P_I) and from the original set of VOCs (P_O). The amount of SOA produced directly from isoprene is

Table 1. Stoichiometric Coefficients, α_i , and Equilibrium Partitioning Coefficients, K_i , for SOA Formation From Low NO_x Chamber Experiments of Reaction of Isoprene With OH^a

Product	α_i	K_i , m ³ μg^{-1} b
1	0.232	0.00862
2	0.0288	1.62

^aSee Kroll *et al.* [2006].

^bReference temperature is 295 K.

6.2 Tg yr⁻¹, almost as large as the original SOA source in the base calculation, 8.7 Tg yr⁻¹. The presence of this much additional organic substrate enhances SOA formation from other sources by 17%. The total SOA burden more than doubles, and the lifetime of the SOA from isoprene (13.5 d) is twice that of the base case SOA (6.7 d). Results from a one month simulation with model resolution of 2° × 2.5° were equivalent.

[12] Two factors give rise to the distinct distributions and lifetimes of the SOA formed from isoprene compared to the base case set of VOCs. Emissions of isoprene are generally much greater. As a result, isoprene is not completely oxidized near its sources, and substantial amounts of isoprene can be lofted to much greater altitudes. Also, gas-particle partitioning of the isoprene oxidation products is shifted less toward the particle phase than that of the products of the base case VOCs; hence, the lifetime of the isoprene oxidation products is also greater. The combined effect of these factors increases SOA precursor concentrations in the free troposphere where partitioning to the aerosol phase is enhanced owing to lower temperatures, leading to formation of SOA in regions where there was little in the base case. Although this increase alone is not enough to account for the discrepancy between predicted and observed tropospheric organic carbon aerosol in the region studied during the ACE-Asia campaign [Heald *et al.*, 2005], it does significantly impact our global picture of organic carbon aerosol distributions.

[13] The total amount of isoprene predicted to be oxidized by OH is 209 Tg yr⁻¹; the global isoprene SOA “yield” is 2.9%, which is essentially the same as those from the low-NO_x chamber experiments (~3%). We find that simply calculating the formation of SOA from isoprene from a direct calculation (wherein SOA is formed, irreversibly, as a constant percentage of the amount of isoprene that reacts) leads to lower SOA burdens than the two-product model, in contrast to previous studies comparing these methods [Lack *et al.*, 2004; Tsigaridis and Kanakidou, 2003]. The reason for this discrepancy is, as noted earlier, a significant portion of the SOA from isoprene is formed from the semivolatile oxidation products that only condense substantially at lower temperatures, an effect that may not be as critical for modeling SOA from sources with greater yields.

[14] We examine SOA levels predicted by the base case model (without isoprene as a source of SOA) when using a reasonably larger value of $\Delta H_v = 50$ kJ mol⁻¹ or when $H =$

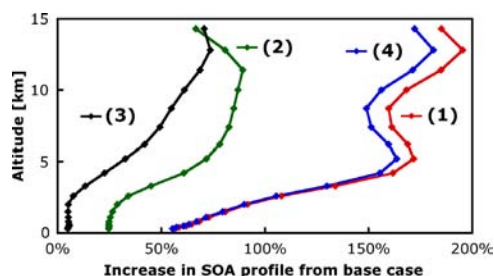


Figure 2. Relative increases in global average SOA concentration profiles with respect to the base case model. Line (1) shows the increase in SOA resulting from including isoprene as a source. The two lines at the left show increases in SOA formed from non-isoprene sources due to line (2) increasing ΔH_v to 50 kJ mol⁻¹ and line (3) decreasing H to 10⁴ M atm⁻¹. Line (4) shows increases in SOA from including isoprene as a source but increasing H to 10⁶ M atm⁻¹.

10⁴ M atm⁻¹. Use of this value of ΔH_v leads to a modest increase in the global SOA burden of 0.08 Tg, and average SOA concentrations in the troposphere increase by a factor of 2 to 3. Decreasing H increases the burden by almost 40%. While these are substantial consequences, the overall magnitude of these effects is still small compared to increases of SOA concentrations from isoprene, as shown in Figure 2. When isoprene is included as a source of SOA, increasing H to 10⁶ M atm⁻¹ has little overall effect, as the oxidation products are effectively completely soluble beyond $H \geq 10^5$ M atm⁻¹.

[15] Including isoprene as a source of SOA causes substantial increases in predicted SOA concentrations, particularly in the free troposphere and remote marine environments. A detailed comparison with measured organic carbon aerosol is now in order. This source of SOA may help explain observations of organic carbon aerosol, noted previously to be under-predicted by this (and others) model in these regions [Heald *et al.*, 2005; Tsigaridis and Kanakidou, 2003], particularly considering recent revisions in estimates of isoprene emissions [Guenther *et al.*, 2006]. This study highlights the need for further research into the chemical fate of the oxidation products of isoprene [Kroll *et al.*, 2006] and the importance of developing SOA models that can explicitly represent condensation of oxidation products normally considered too volatile to contribute to organic aerosol formation [Donahue *et al.*, 2006]. These results may have implications for climate change given the magnitude of the predicted top of the atmosphere radiative forcing of organic carbon in year 2100 climate [Liao *et al.*, 2006].

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References

- Calvert, J., R. Atkinson, J. Kerr, S. Madronich, G. K. Moortgat, T. Wallington, and G. Yarwood (2000), *The Mechanisms of Atmospheric Oxidation of the Alkenes*, Oxford Univ. Press, New York.
- Chung, S. H., and J. H. Seinfeld (2002), Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.*, 107(D19), 4407, doi:10.1029/2001JD001397.

Table 2. Summary of Yearly SOA Production Rates and Average Burdens as a Function of SOA Sources, SOA Enthalpy of Vaporization (ΔH_v), and the Henry's Law Constant of the Oxidation Products (H)

Source ^a	ΔH_v , kJ/mol	H , M/atm	P_O , Tg/yr	P_I , Tg/yr	P_T , Tg/yr	B_T , Tg
<i>O</i>	42	10 ⁵	8.7	-	8.7	0.16
<i>O + I</i>	42	10 ⁵	10.2	6.2	16.4	0.39
<i>Sensitivity Calculations</i>						
<i>O</i>	50	10 ⁵	11.1	-	11.1	0.24
<i>O</i>	42	10 ⁴	9.7	-	9.7	0.22
<i>O + I</i>	42	10 ⁶	10.1	6.1	16.2	0.38

^a*I* = isoprene, *O* = other biogenic VOC's.

- Claeys, M., W. Wang, A. C. Ion, I. Kourtev, A. Gelencser, and W. Maenhaut (2004a), Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, *Atmos. Environ.*, **38**, 4093–4098.
- Claeys, M., et al. (2004b), Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, **303**, 1173–1176.
- Czochke, N. M., M. Jang, and R. M. Kamens (2003), Effect of acidic seed on biogenic secondary organic aerosol growth, *Atmos. Environ.*, **37**, 4287–4299.
- Donahue, N. M., A. L. Robinson, C. O. Stanier, and S. N. Pandis (2006), The coupled dilution, partitioning, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, doi:10.1021/es052297c.
- Edney, E. O., T. E. Kleindienst, M. Jaoui, M. Lewandowski, J. H. Offenberg, W. Wang, and M. Claeys (2005), Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States, *Atmos. Environ.*, **39**, 5281–5289.
- Griffin, R. J., D. R. Cocker, R. C. Flagan, and J. H. Seinfeld (1999a), Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, **104**, 3555–3567.
- Griffin, R. J., D. R. Cocker, J. H. Seinfeld, and D. Dabdub (1999b), Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, **26**, 2721–2724.
- Guenther, A., et al. (1995), A global-model of natural volatile organic-compound emissions, *J. Geophys. Res.*, **100**, 8873–8892.
- Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. I. Palmer, and C. Geron (2006), Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys. Discuss.*, **6**, 107–173.
- Heald, C. L., D. J. Jacob, R. J. Park, L. M. Russell, B. J. Huebert, J. H. Seinfeld, H. Liao, and R. J. Weber (2005), A large organic aerosol source in the free troposphere missing from current models, *Geophys. Res. Lett.*, **32**, L18809, doi:10.1029/2005GL023831.
- Ion, A. C., R. Vermeylen, I. Kourtev, J. Cafmeyer, X. Chi, A. Gelencser, W. Maenhaut, and M. Claeys (2005), Polar organic compounds in rural PM_{2.5} aerosols from K-puszt, Hungary, during a 2003 summer field campaign: Sources and diurnal variations, *Atmos. Chem. Phys.*, **5**, 1805–1814.
- Kanakidou, M., et al. (2005), Organic aerosol and global climate modeling: A review, *Atmos. Chem. Phys.*, **5**, 1053–1123.
- Kourtev, I., T. Ruuskanen, W. Maenhaut, M. Kulmala, and M. Claeys (2005), Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiälä, Finland, *Atmos. Chem. Phys.*, **5**, 2761–2770.
- Kroll, J. H., N. L. Ng, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2005), Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions, *Geophys. Res. Lett.*, **32**, L18808, doi:10.1029/2005GL023637.
- Kroll, J. H., N. L. Ng, S. M. Murphy, R. C. Flagan, and J. H. Seinfeld (2006), Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, **40**, 1869–1877, doi:10.1021/es0524301.
- Lack, D. A., X. X. Tie, N. D. Bofinger, A. N. Wiegand, and S. Madronich (2004), Seasonal variability of secondary organic aerosol: A global modeling study, *J. Geophys. Res.*, **109**, D03203, doi:10.1029/2003JD003418.
- Liao, H., W.-T. Chen, and J. H. Seinfeld (2006), Role of climate change in global predictions of future tropospheric ozone and aerosols, *J. Geophys. Res.*, doi:10.1029/2005JD006852, in press.
- Lim, H. J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, **39**, 4441–4446.
- Limbeck, A., M. Kulmala, and H. Puxbaum (2003), Secondary organic aerosol formation in the atmosphere via heterogeneous reaction of gaseous isoprene on acidic particles, *Geophys. Res. Lett.*, **30**(19), 1996, doi:10.1029/2003GL017738.
- Matsunaga, S., M. Mochida, and K. Kawamura (2003), Growth of organic aerosols by biogenic semi-volatile carbonyls in the forestal atmosphere, *Atmos. Environ.*, **37**, 2045–2050.
- Matsunaga, S., C. Wiedinmyer, A. B. Guenther, J. J. Orlando, T. Karl, D. W. Toohey, J. P. Greenberg, and Y. Kajii (2005), Isoprene oxidation products are a significant atmospheric aerosol component, *Atmos. Chem. Phys. Discuss.*, **5**, 11,143–11,156.
- Odum, J. R., T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan, and J. H. Seinfeld (1996), Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, **30**, 2580–2585.
- Offenberg, J. H., T. E. Kleindienst, M. Jaoui, M. Lewandowski, and E. O. Edney (2006), Thermal properties of secondary organic aerosols, *Geophys. Res. Lett.*, **33**, L03816, doi:10.1029/2005GL024623.
- Park, R. J., D. Jacob, B. D. Field, R. Yantosca, and M. Chin (2004), Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, *J. Geophys. Res.*, **109**, D15204, doi:10.1029/2003JD004473.
- Seinfeld, J. H., and J. F. Pankow (2003), Organic atmospheric particulate material, *Annu. Rev. Phys. Chem.*, **54**, 121–140.
- Tsigaridis, K., and M. Kanakidou (2003), Global modeling of secondary organic aerosol in the troposphere: A sensitivity analysis, *Atmos. Chem. Phys.*, **3**, 1849–1869.

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